Contribution from the Physical Chemistry Laboratory,
Swiss Federal Institute of Technology Zurich, Switzerland and
Shell Development Company, Emeryville, California, U.S.A.

Detection of an Intermediate, Five-Coordinated Monopyridine Adducts of Square-Planar Nickel(II) Chelates in the Presence of Pyridine

Gerd N. La Mar

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The paramagnetic, mono-pyridine adducts of the square-planar, diamagnetic bis(N-alkyl salicylaldimine)nickel(II) chelates in the presence of pyridine have been detected by proton magnetic resonance. Detection was made possible by the fact that the spin delocalization mechanisms to the aromatic chelate ring differed significantly in the five-coordinated, mono-pyridine adduct and the six-coordinated, di-pyridine adduct.

Introduction

A number of square-planar, diamagnetic nickel complexes undergo a reaction in pyridine solution, where two solvent molecules are coordinated to form a stable, paramagnetic diadduct.[1,2] Presumably the reaction proceeds via a five-coordinated intermediate, which has a sufficiently short lifetime or exists in a small enough concentration so as to make detection of the mono-pyridine adduct very difficult.[2,3] In particular, the bis(N-substituted salicylaldimine)Ni^{II} chelates,[4] designated N(R)NiSAL, readily form the di-pyridine adducts, but the mono-adduct intermediate has not been detected,[2] though for the analogous Co^{II} chelates, five-coordinated mono-adducts have been detected optically, and even isolated in certain cases.[3,5]

It is our purpose here to demonstrate that evidence for the existence of the intermediate, five-coordinated mono-pyridine adducts of N(alkyl)NiSAL can be derived from a ligand proton magnetic resonance investigation. Both the mono-pyridine,[6a] as well as the di-pyridine adducts,[6b] are expected to be paramagnetic ($S=1$), and thus exhibit isotropic shifts for the ligand protons.[7-11] If the spin delocalization mechanisms in the five-and six-coordinated complexes are sufficiently different,[12] the presence of even a small fraction of the intermediate mono-adduct may be detected.

Experimental Section

N(ethyl)NiSAL and N(*n*-propyl)NiSAL were dissolved in d-chloroform or carbon disulfide (0.1 *M*), and increasing amounts of d_5-pyridine were added. The proton nmr trace was recorded after each addition of pyridine until further pyridine had no effect on the spectrum. Deuterated pyridine was necessary, since an excess of the undeuterated pyridine obscured the NiSAL ligand resonances. The proton spectra for each complex in pure d_5-pyridine were also recorded.[13]

Attempts to obtain similar proton spectra of bis(pyrrole-2-aldimine)Ni^{II}[14] resulted in decomposition of the chelate, while bis(N-methyl aminotroponeimine)-Ni^{II}[15] failed to react with pyridine.

The proton spectra were recorded on a Varian DP-60 spectrometer, operating at 29°, and using TMS as internal calibrant. The isotropic shifts are defined as the difference between the observed shifts in the paramagnetic complex and the diamagnetic chelate.

Results and Discussion

The dependence of the ligand proton shifts on the pyridine concentration for N(ethyl)NiSAL is illustra-

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(1) F. Basolo and W. Matoush, *J. Am. Chem. Soc.*, *75*, 5683 (1953); H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955); R. H. Holm, *J. Am. Chem. Soc.*, *83*, 4683 (1961); A. Chakravorty, T. S. Kannan, and S. Gupta, *Inorg. Nucl. Chem. Letters*, *4*, 139 (1968).

(2) S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi, and K. Iwasaki, *Coord. Chem. Rev.*, *3*, 247 (1968).

(3)The mono-pyridine adduct of bis (diethyldithiophosphate)Ni(II) has been detected optically, and the equilibrium constants for the formation of the two adducts determined. R. L. Carlin, J. S. Dubnoff, and W. T. Huntress, *Proc. Chem. Soc.*, 228 (1964).

(4) L. Sacconi, P. Paoletti, and G. Del Re, *J. Am. Chem. Soc.*, *79*, 5062 (1957).

(5) S. Yamada, and H. Nishikawa, *Bull. Chem. Soc. Japan*, *38*, 683 (1965); S. Yamada and E. Yoshida, *Bull. Chem. Soc. Japan*, *40*, 1298, 1854 (1967).

(6) (a) Previous investigations on five coordinated nickel(II) complexes has shown that with the donor atoms O_2N_3, the complexes are always paramagnetic, so that the assumption of a paramagnetic mono-pyridine adduct is reasonable (L. Sacconi, in «Transition Metal Chemistry, R. L. Carlin, Ed., M. Dekker, New York, 1968, pp. 199-298, particularly p. 220). (b) J. D. Thwaites and J. P. Porchet, private communication.

(7) D. R. Eaton and W. D. Phillips, *Adv. Mag. Res.*, *1*, 103 (1965).

(8) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, *86*, 379 (1964).

(9) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, *4*, 26 (1965).

(10) J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, *5*, 1029 (1966); J. D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, *5*, 1036 (1966).

(11) G. N. La Mar and L. Sacconi, *J. Am. Chem. Soc.*, *89*, 2282 (1967).

(12) G. N. La Mar, *Mol. Phys.*, *12*, 427 (1967).

(13) That only the di-adduct is present in pure d_5-pyridine is verified by the independence of the observed contact shifts of the concentration of the complex.

(14) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, *5*, 625 (1965).

(15) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, *85*, 397 (1963).

ted in Figure 1. As previously observed for pyridine adducts,[16,17] the rate of pyridine exchange is sufficiently fast to produce only an averaged proton spectrum[18] at all pyridine concentrations. Though it has been reported that all the N(alkyl)NiSAL chelates associate slightly in non-donor solvents,[4] the proton spectrum in the absence of pyridine gave no evidence whatsoever for any isotropic shifts at the concentrations studied, and closely resemble the proton spectra of the analogous diamagnetic zinc chelates.[10,11] Spin-spin splittings for all but the azomethine proton permitted the assignments[7-9] of the diamagnetic resonances. The multiplet patterns were maintained until the peaks were shifted 1-3 ppm, and thereby permitted an unambiguous assignment[17] of all resonances by following the shift of any resonance as a function of pyridine concentration. The contact shifts for the magnetically isotropic di-pyridine adduct closely resemble the spin distributions reported for other six-coordinated NiSAL complexes.[9,12]

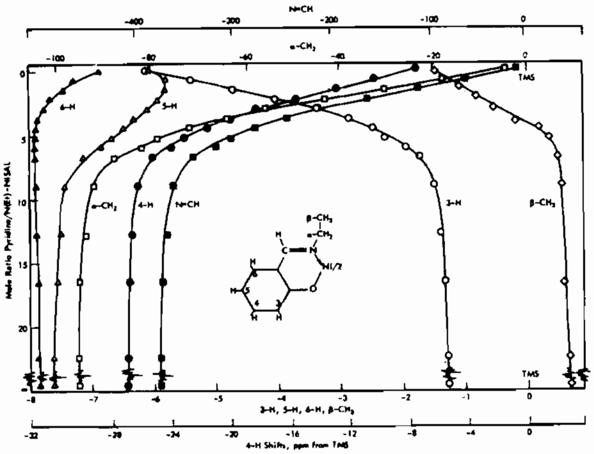

Figure 1. Dependence of Contact Shifts of N(Et)—NiSAL in $CDCl_3$ on Pyridine/Complex Ratio, in ppm, Referenced to TMS.

For a simple system, where one square-planar, diamagnetic complex reacts with two molecules of pyridine to form the di-adduct as the only paramagnetic species, the averaged contact shift will increase monotonically with increasing pyridine concentration, from zero in the absence of pyridine, to the value for the pure di-adduct in d_5-pyridine solution. However, if a third, paramagnetic species exists that can participate in an equilibrium with both the diamagnetic chelate and its di-adduct, then this simple contact shift behavior will not be observed if the third species in solution has a spin density distribution which markedly differs from that of the diadduct.

Inspection of Figure 1 reveals that for 3-H, 4-H, N=CH, and α-CH_2, ostensibly « normal » behavior is observed. However, for the 5-H, the contact shift first increases in a positive direction to a maximum of +0.3 ppm, and then decreases to a negative value in the di-adduct as the pyridine concentration is increased. Also, for 6-H, the contact shift appears to increase at a much faster rate than for the other protons, reaching a maximum of −1.15 ppm, and then decreasing slightly to −1.1 ppm in the di-adduct. An identical behavior is observed for the N(*n*-propyl)-NiSAL complex upon adding pyridine, though the additional methylene protons interfered with the unambiguous identification of the 3-H peak at pyridine/complex ratios exceeding ~5. The N(methyl)-NiSAL complex is primarily associated[4] in $CDCl_3$, and hence it was impossible to locate the peaks under any circumstances except in the di-pyridine adduct.

Table I. Calculated Percent Paramagnetic Adduct from Observed Shifts.[a]

Pyridine/Complex	3-H	4-H	5-H	6-H
0.7	15.8	14.3	[b]	37.9
1.5	29.3	27.0	[b]	54.6
2.3	43.0	41.6	[b]	74.2
3.0	56.9	55.4	2.0	84.8
3.8	67.3	64.3	16.2	93.9
4.5	75.7	73.0	26.3	95.4
5.3	79.7	80.2	39.4	95.4
6.0	83.7	84.3	48.4	98.7
7.5	90.9	91.2	67.7	102.0
9.8	96.1	96.1	84.4	101.2
12.8	98.0	98.0	90.0	100.0
∞	100.0	100.0	100.0	100.0

[a] The percent adduct formation is calculated by dividing the observed averaged shift by the contact shift of the di-adduct in d_5-pyridine solution at 29°. [b] Positive shifts observed, as shown in Figure 1, while the di-adduct contact shift is negative.

If only the diamagnetic chelate and its di-adduct are present in solution, then the observed contact shift for a given pyridine/NiSAL ratio divided by the contact shift of the di-adduct will yield the fractional adduct formation, and this fraction should be independent of which contact shift is used in the calculation. Table I illustrates the percent di-adduct formation calculated by this method for the aromatic ring protons. As an example, when the 6-H shift indicates ~95% reaction, the 5-H gives only ~25%, while the 4-H yields ~75% di-adduct formation. On the other hand, the percent di-adduct based on 3-H, 4-H, α-CH_2 and N=CH are essentially the same .

Since the positive 5-H shift appears only at very low pyridine concentration, with its maximum at pyridine/NiSAL = 1, it is considered likely that the third paramagnetic species is the mono-pyridine adduct, which would be five-coordinated and probably paramagnetic.[6a,11]

An alternative explanation to the five-coordinated mono-adduct would be that the intermediate species is the *cis* di-adduct, which converts to the *trans* isomer in excess pyridine. This second possibility is considered unlikely for the following reasons:

(a) The same contact shift dependence on pyridine concentration for 5-H and 6-H as shown in Figure 1

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[16] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 39, 1211 (1963).
[17] G. N. La Mar, *Inorg. Chem.*, 8, 581 (1969)
[18] The average isotropic shift therefore represents a weighted average of the contributing paramagnetic species, since the diamagnetic chelate has zero isotropic shift by definition.

is observed for N(n-propyl)-NiSAL, although the change in the size of the alkyl substituent might be expected to alter the relative stabilities of the *cis* and *trans* isomers in solution.

(b) It has been shown that the spin delocalization in the acetylacetone (AA) ion in $(AA)_2Ni^{II}X_2$ is independent of whether the complex exists in the *trans*[19a] or the *cis*[19b] configuration, so that significant differences in contact shifts for the two isomers are not expected for the present system.

(c) Assuming that the 4-H contact shift in the intermediate species and di-adduct are very similar, it is estimated that the 5-H contact shift for the former species is $> +3.0$ ppm, compared to the -1.65 ppm contact shift for di-adduct. Previous investigations[10] of spin delocalization in *cis* and *trans* isomers of the same complexes do not lead us to expect such a sizable difference in spin densities between the two isomers, particularly with a reversal of shift direction.

(d) The presence of the mono-pyridine adduct is indicated by the transient band observed at 13,500 cm^{-1} for the related N(2,6-dimethylphenyl)-NiSAL chelate.[21]

Finally, it will be shown below that the observed deviations of the contact shifts with pyridine concentration are consistent with the behavior expected for an intermediate, five-coordinated species.

Considerable attention has been focused on elucidating the spin delocalization mechanisms in NiSAL complexes,[8,12] and it has been shown that different contact shift patterns characterize the coordination numbers four,[8] five,[11,12] and six.[9,12] Dipolar shifts have been shown to be negligible in all NiSAL chelates.[8,12] The contact shift pattern for five-coordinated NiSAL is quite insensitive to the exact structure of the chelate,[11,12] and differs significantly from the pattern for six-coordinated complexes. If we assume that the previously observed[11] shift pattern for the five-coordinated chelates is roughly diagnostic for the coordination number, we expect the mono-pyridine adduct to display ring contact shifts[22] $+18/-19/+6/-8$ ppm for the 3-H/4-H/5-H/6H, respectively. The observed contact shifts for the present di-pyridine adduct are $+5.1/-19.4/-1.65/-1.1$ ppm, for the analogous ring protons. The *difference* in contact shif patterns anticipated between the mono-and di-pyridine adducts can thus be expressed as the ratio of proton shifts in the former to those of the latter adduct, which are calculated to be $3.5/1.0/-3.5/7.2$ for 3-H/4-H/5-H//6-H. The presence of the five-coordinated intermediate will therefore affect the contact shift pattern of the di-adduct primarily at the 5-H, less at the 6-H, and perhaps only indetectibly at 3-H. The 4-H shifts should be very similar for both adducts.

Since the 4-H shift is expected to be essentially identical for the mono- and di-adduct, the percent adduct formation in Table I for this position should be a good index of the fraction of paramagnetic complexes, whether mono- or di-adduct. If the contact shift for a given proton in the five-coordinated species is expected to be larger (smaller) than in the octahedral di-adduct, then the calculated percent adduct formation for a given pyridine/NiSAL in Table I for that proton should be larger (smaller) than that obtained from the 4-H contact shift. The data in Table I show this behavior for each of the aromatic protons at low pyridine/NiSAL ratios; the deviations are largest for 5-H and 6-H, as can be seen in Figure 1, but they are also noticeable for 3-H in Table I. Thus the magnitude of the deviations from the behavior expected for only the di-adduct correlate well with the relative differences in contact shifts between the di-adduct and the previously reported five-coordinated NiSAL complexes.[11,12]

The N=CH, α–CH_2, and β–CH_3 shifts for the di-adduct, -360, -90, and $+2.22$ ppm, respectively, are very similar to some of those observed for the five-coordinated chelates,[11] -280, -70 to -100, and $+1.0$ to $+8.0$ ppm, respectively, so their contact-shift dependence on pyridine would be expected to be nearly the same as that for 4-H, as is observed.

When N(Et)–NiSAL is dissolved in carbon disulfide instead of chloroform, the contact-shift behavior with added pyridine is similar to that shown in Figure 1, except that the maximum positive 5-H contact shift is smaller, only ~ $+0.2$ ppm, and the deviations for the 6-H shift are not as obvious as in Figure 1. This suggests that for a given pyridine/NiSAL ratio, the mono-adduct is less stable in CS_2 than $CDCl_3$. This effect could well result from the more favorable dielectric or solvating properties of $CDCl_3$ relative to CS_2.

Since the exact magnitudes of the contact shifts for the mono-adduct are not known, it is not possible to calculate the equilibrium constants[3] at this time. This case does demonstrate, however, that the presence of transient paramagnetic species in the presence of another paramagnetic complex can be detected by proton magnetic resonance if the contact shift pattern for the contributing paramagnetic species differ sufficiently.

For the pyridine adducts of the bis(β-ketomimine)-Ni^{II} and bis(monothio-acetylacetonate)Ni^{II} chelates, the failure to detect[17] any anomalous contact shift behavior at low pyridine/complex ratios could result from either the lack of a significant amount of the mono-pyridine adduct, or, more likely, from the fact that the spin delocalization mechanisms for the two adducts are too similar.

The recent X-ray structure determination[23] for N(ethyl)NiSAL has shown that the diamagnetic complex is not planar, but adopts a « stepped » structure, where the aromatic planes are inclined at an angle of ~23° to the NiO_2N_2 plane. The π spin density observed for the di-adduct therefore probably arises

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(19) (a) G. N. La Mar, *J. Mag. Res.*, *1*, 186 (1969). (b) The contact shifts for the AA protons (AA=acetylacetonate) in the presumable *trans* $Ni(AA)_2 \cdot 2Py$ and the necessarily *cis* $Ni(AA)_2 \cdot Bipy$ (Bipy = bipyridine) are essentially identical (G. N. La Mar, unpublished observations).

(20) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, *6*, 1315 (1967); *Inorg. Chem.*, *6*, 1607 (1967); *J. Am. Chem. Soc.*, *89*, 6472 (1967).

(21) L. Sacconi, private communication. This complex failed to produce a detectable proton spectrum at the concentration at which the ligand field band has been observed.

(22) These shifts, taken from Ref. 11, are typical for the *five*-coordinated chelates $[(-O-C_6H_4-CH=NCH_2CH_2CH_2-)_2NH]Ni^{II}$, where the small splittings due to ring inequivalence have been averaged.

not from direct π delocalization, but from the expected σ spin delocalization, which is transferred to the π system within the ligand, due to the non-orthogonality[23] of the ligand σ and π systems. It appears unnecessary to invoke significant unpairing of the paired t_{2g}^{π} electrons to account for the shifts.[12]

Acknowledgments. The support of NATO through a Postdoctoral Fellowship at the SFIT is gratefully acknowledged.

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(23) L. M. Shkol'nikova, A. N. Knyazeva, and V. A. Voblikova, *J. Struct. Chem.* (USSR), *8*, 77 (1967). [*Zh. Strukt. Khim.*, *8*, 94 (1967)].